JOINT INSTITUTE FOR LABORATORY ASTROPHYSICS

UNIVERSITY OF COLORADO
BOULDER, COLORADO 80309

UNIVERSITY OF COLORADO

NATIONAL BUREAU OF STANDARDS

LEVEL II

12

SEMIANNUAL REPORT

RESEARCH IN LASER PROCESSES

Research Sponsored by
Advanced Research Projects Agency
and
Office of Naval Research

ARPA Order No. 2683, Amendment 6
Program Code No. 8E20
Contractor: University of Colorado
Effective Date of Contract: 1 July 1975
Contract Expiration Date: 15 Nov. 1978
Amount of Contract: $480,000
Period Covered: 1 August 1977 to
31 January 1978

Contract No. N00014-76-C0123
Principal Investigators:
A.V. Phelps
Telephone: (303) 492-7850
A.C. Gallagher
Telephone: (303) 492-7841
Scientific Officer: Director,
Physics Program, ONR
Short Title of Work: Laser Processes

28 April 1978

Cable Address: JILA

Telephone Number: 492-7789

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: None	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): Semiannual Report		5. TYPE OF REPORT & PERIOD COVERED: Semiannual Report, 1 August 1977 to 31 Jan. 1978
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): A. V. Phelps and A. C. Gallagher		8. CONTRACT OR GRANT NUMBER(s): N00014-76-C-0123, ARPA Order-2683
9. PERFORMING ORGANIZATION NAME AND ADDRESS: University of Colorado, Joint Institute for Laboratory Astrophysics, Boulder, C 80309		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 393-506/12-09-77, Code 421; ARPA Ord No. 2683, Amd. 6, Prog. Cd. 8E20
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Department of the Navy, 800 North Quincy St., Arlington, VA 22217		12. REPORT DATE: 28 April 1978
		13. NUMBER OF PAGES: 20 p.
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report): Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Research in Laser Processes.

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Laser, processes, sodium vapor, rare gas, electrical discharge, high pressure, molecules, metastables.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The optical properties of electrical discharges in high pressure Na-Xe mixtures which are being evaluated for laser applications have been modeled. These models lead to the proposal that suitability of electrical discharge excitation for a metal vapor based excimer laser depends critically on the dissociative recombination coefficient for electrons and the dominant positive ion. Such a model can account for the low excited atom densities found previously in our NaXe experiments. The theoretical predictions of low optical pumping efficiency at the center of the resonance lines (continued over)

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE

to next page

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

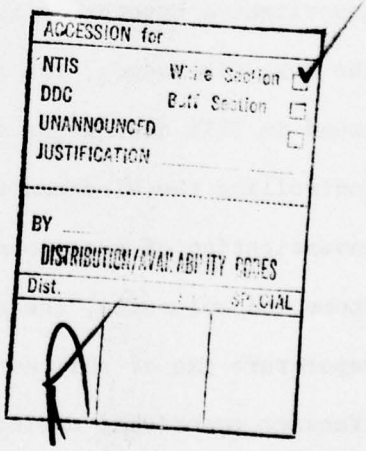
have been verified for the D_1 and D_2 lines of Na vapor, i.e., the fluorescence efficiency decreases to about 7% at line center for a sodium density of 10^{15} atom/cm^3. Much improved measurements have been made of collisional relaxation rate coefficients for the v=0 and v=1 vibrational levels of the N_2 ($A^3\Sigma_u^+$) state.

A sub 1 3 Sigma (+) sub u

10 to the 15th power

SEMIANNUAL REPORT

This Semiannual Report contains descriptions of work carried out under ONR Contract No. N00014-76-0123 and ARPA Order No. 2683-Amd. 6. It covers the period from 1 August 1977 to 31 January 1978. Section I is the Semiannual Report Summary while Sections II-IV are more detailed descriptions of work carried out under the three projects supported by this contract.



I. SEMIANNUAL REPORT SUMMARY

The three projects in the area of Laser Process being carried out under this contract are summarized below. More detailed discussions are given in Sections II through IV of this report.

(1) Metal Vapor-Rare Gas Discharges.

The objective of this project is the evaluation of the potential of electrical discharges in high pressure metal vapor-rare gas mixtures for the excitation of high power, high efficiency lasers operating at near visible wavelengths. Our previous work has shown that many metal vapor-rare gas excimers have reasonable stimulated emission coefficients at visible or near visible wavelengths and that electrical discharges with sufficiently high electron temperatures (>0.5 eV) should be an efficient way to produce these excimers. Our recent experiments have shown that the effective electron temperature in high power ($\sim$30 kW/cm^3 at 3 atm. pressure) discharges in Na-Xe mixtures is too low ($\sim$0.4 eV) to yield gain on the NaXe excimer transition. Work carried out during this report period has resulted in a quantitative hypothesis as to the reason for the low electron temperature in the NaXe discharges, the significantly higher apparent electron temperature found in TℓXe discharges in another investigation, and the molecular processes controlling the electron temperature. This work leads us to urge vigorous investigation of processes such as the electron excitation of highly excited atoms and molecules, the dissociative recombination of electrons and metal vapor-rare gas or related hetronuclear molecular ions, molecular ion-atom transfer reactions, excited state quenching processes, etc. Our planned approach to these processes is primarily via comparison of discharge based experiment and models, but there is an urgent need for the study of energy dependences, etc. of the isolated processes.

(2) Transport of Resonance Excitation in Gases.

These experiments are designed to test our ability to predict the decrease in pumping efficiency which occurs when a metal vapor is excited by a laser tuned to frequencies near that of the center of the resonance line. At moderate and high metal vapor densities this loss is caused primarily by the nonradiative transport of resonance atom excitation to the entrance window. Although our measurements cover only a limited range of metal vapor densities they show the expected large decreases in pumping efficiency and suggest that our theory can usefully be extended to high densities, e.g., to $\sim 10^{18}$ atom/cm^3 in Na vapor.

(3) Electron Excitation of Metastable Atoms and Molecules.

The technical problem addressed in this project is the measurement and prediction of rate coefficients for the electron excitation of the $A^3\Sigma_u^+$ metastable state of N_2 and the metastable states of Ar. The metastable N_2 molecules have been suggested by DoD contractors as an efficient source of excitation for the upper laser levels of molecules and atoms, such as NO and Hg, while the Ar metastable states are one of the two important sources of excitation in most KrF and XeF lasers, e.g., those utilizing discharge enhancement in mixtures of Ar, Xe and F_2. Measurements defining the kinetics of the metastables in pure N_2 have been completed. Analysis of the $N_2(A^3\Sigma_u^+)$ excitation data have required measurement of the rate and efficiency of deexcitation of the v=1 level to the v=0 level of the $A^3\Sigma$ state. Also, since the decay of the v=1 level density is surprisingly sensitive to the presence of either excited N_2 or N atoms the measurements had to be made at very low electron densities and signal levels.

II. METAL VAPOR-RARE GAS DISCHARGES

Drs. W. L. Morgan, H. Rothwell (to 9/77), R. Shuker, L. Shumann (from 9/77), A. Gallagher and A. V. Phelps and Mr. D. Leep (to 9/77).

The principal objective of this project during this report period has been to understand the reasons for the low ratios of excited state densities to ground state density measured in the NaXe discharges which we have been evaluating for high power laser applications. As discussed in the last Semiannual Report our measurements show that in these discharges the excited state and apparent electron temperatures reach only about 0.4 eV at current densities of about 150 A/cm^2. Since our experiments under another contract in TlXe mixtures sometimes show a favorable non-Boltzmann distribution of excited state populations we are engaged in an extensive effort to understand the factors which control the distribution in energy of excited state populations. The experimental results obtained during this report period have not shown any qualitatively different behavior than earlier results. We will therefore limit this report to the conclusions drawn from the comparisons of our models with the data reported previously.

Figure 1 shows the energy levels and principal collision processes considered in our most recent models. This diagram differs from that shown previously in that a) many more excited states of Na are considered important because of the large rate coefficients for electron collisions which excite and deexcite these levels, b) negligible dissociative recombination is believed to occur as the result of collisions between electrons and $NaXe^+$ ions and c) the excited atomic states of Na produced by dissociative recombination of an electron and Na_2^+ are believed to be much closer to the ionization level and d) the conversion of $NaXe^+$ ions to Na_2^+ ions in collisions with Na atoms has become a rate limiting step in the control of electron density by recombination. The theoretical prediction of the absence of dissociative

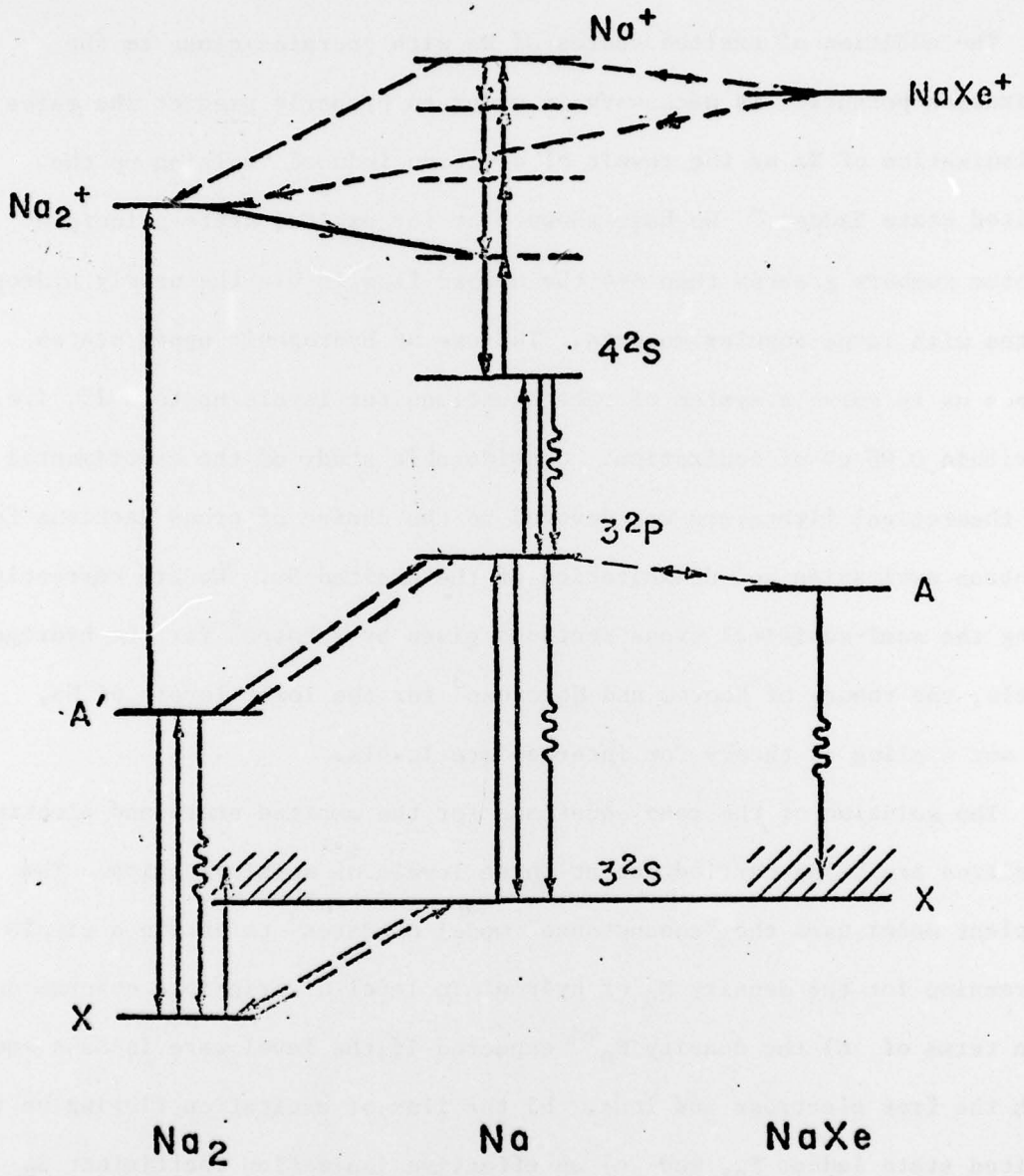


Figure 1. Energy levels and principal processes for high power electrical discharges in Na-Xe mixtures at high pressures. Processes code: solid lines are electron collision induced, dashed lines are neutral collision induced and wavey lines are radiative transitions.

recombination for alkali-rare gas ions such as $NaXe^+$ was made by Biondi[1] during this report period. The consequences of the deletion of this process are still being investigated and will be presented in only a general fashion in this report.

The addition of excited states of Na with energies close to the ionization potential is necessary in order to properly predict the rates of ionization of Na as the result of electron induced "walking up the excited state ladder." We have shown that for excited state principle quantum numbers greater than n=4 the upward flow is via the nearly hydrogenic states with large angular momenta. The use of hydrogenic upper states allows us to solve a system of rate equations for levels up to n=15, i.e., to within 0.06 eV of ionization. Considerable study of the experimental and theoretical literature was devoted to the choice of cross sections for electron excitation and deexcitation of the excited Na. We are currently using the semi-empirical cross sections given by Johnson[2] for the hydrogenic levels, the theory of Moores and Norcross[3] for the lower levels of Na, and our scaling of theory for intermediate levels.

The solution of the rate equations for the excited state and electron-ion densities are being carried out at three levels of sophistication. The simplest model uses the "conductance" model of Bates[4] to obtain a simple expression for the density N_n of hydrogenic level of principle quantum number n in terms of a) the density N_n^{eq} expected if the level were in Saha equilibrium with the free electrons and ions, b) the flux of excitation flowing up the excited state ladder F_n, and c) an effective ionization coefficient S_n calculated as described by Bates[4] from the individual electron deexcitation rate coefficients. This relation is

$$\frac{N_n}{N_n^{eq}} = 1 + \frac{F_n}{S_n n_e} ,$$

where n_e is the electron density. This model neglects radiative and gas collision included transitions between levels of the ladder and assumes that the only important electron induced transitions are between adjacent hydrogenic levels, i.e., $n \rightarrow n \pm 1$. This model is useful for determining approximate excited state densities when a more extensive model shows that the flux F_n is determined by the dissociative recombination rate or some other rate limiting process.

The second level of sophistication, and the most extensively pursued, is that in which a rate equation is written for each of the excited states, ions and free electrons. The results of solutions of the rate equations for the lower four excited states for the NaXe system were discussed in an earlier Semiannual Report. Our present model includes 19 excited states, 5 charged species, and roughly 400 rate coefficients. This model can be greatly simplified once the dominant collision processes appropriate to a given gas mixture and range of discharge conditions are identified. Thus, in the energy level diagram of Fig. 1 the upward flowing flux F_n is equal to the downward flux which bypasses the excited state ladder. In this model Na^+ ions are first converted into Na_2^+ ions and then dissociatively recombine with electrons to form excited Na. The ion conversion can occur in either three-body collisions with Na and Xe atoms or, more likely, in a three-body collision with two Xe atoms to form $NaXe^+$ followed by an atom exchange collision with an Na atom to form the Na_2^+. For most of the conditions of interest to us the rate limiting step in this process is that of the atom exchange, i.e., $NaXe^+ + Na \rightarrow Na_2^+ + Xe$. In these cases the Na_2^+ density adjusts to a value such that the rate of dissociative recombination equals the rate of Na_2^+ formation.

The excited state densities calculated using a variation of our model which includes dissociative recombination of $NaXe^+$ to examine the effect of large changes in the dissociative recombination process are shown in Fig. 2. In both of these calculations the dissociative recombination occurred

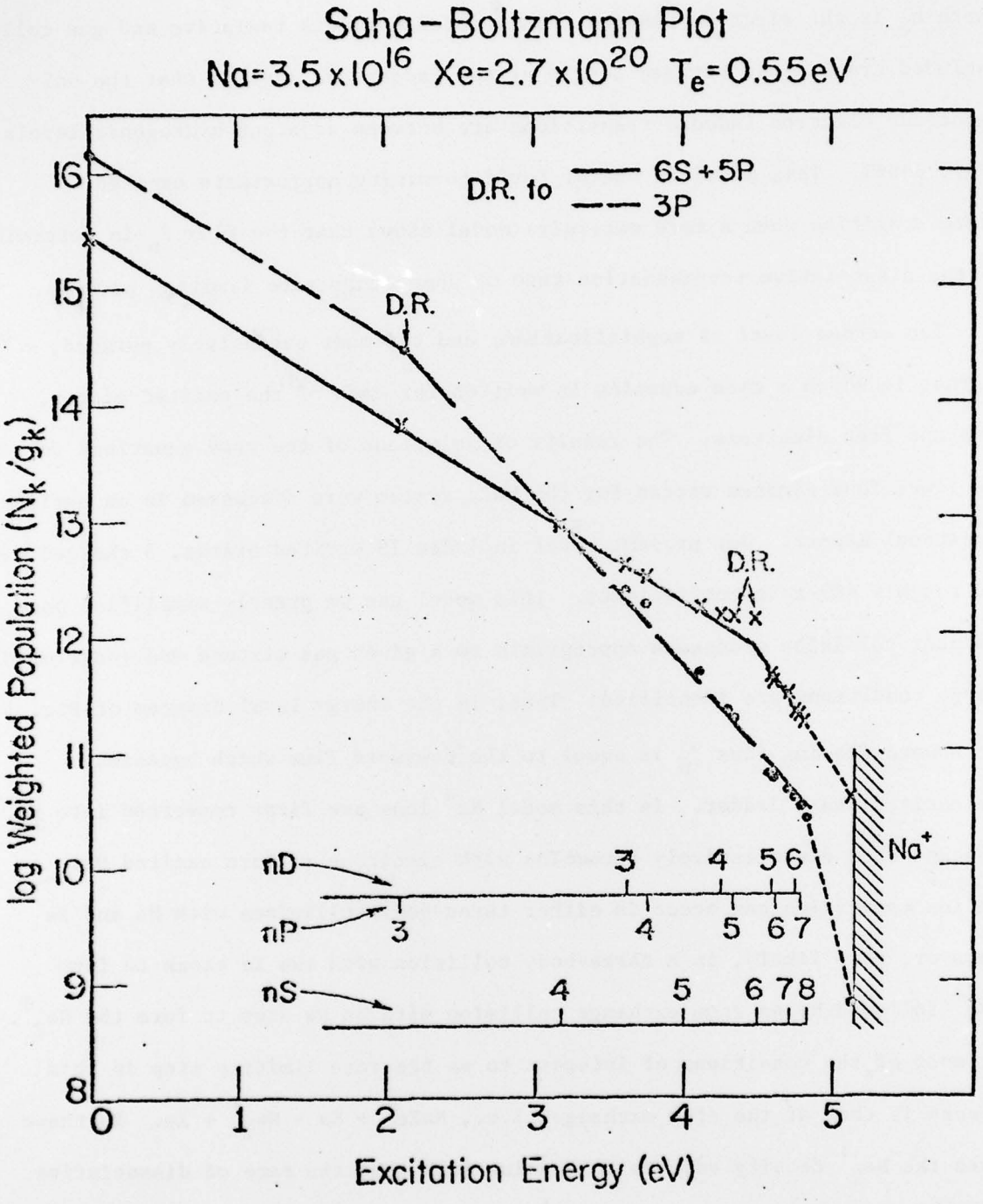


Figure 2. Calculated ground and excited state populations normalized to their statistical weights vs. excitation energy for [Na] = 3.5×10^{16} cm^{-3}, [Xe] = 2.7×10^{20} cm^{-3} and T_e = 0.55 eV. For Saha equilibrium all points would lie on a wtraight line with a slope corresponding to 0.55 eV. The points at 5.1 eV represent the appropriately normalized product of the electron and Na^+ densities.

via the $NaXe^+$ ion but the energy of the resulting excited sodium atoms was much different. Thus, the solid curve and crosses are obtained when the products of dissociative recombination are Na atoms in the 5P and 6S levels, while the dashed curve and dots are obtained when Na atoms in the 3P state are produced. Of particular interest for laser applications is the significantly higher excited state density, lower ground state depletion and the much lower electron density and resultant higher and more favorable discharge impedance in the case with dissociation to the lower excited state.

Figure 3 shows the results of a calculation with the same model as for the crosses in Fig. 2 except that the electron temperature has been lowered to one of the experimental values reported in the last Semiannual Report. We see that it is possible to choose the magnitude of the dissociative recombination coefficient (3.8×10^{-8} cm^3/sec at 0.38 eV) and the product excited state so as to fit the experimental data. Although at the time of this report we had not obtained such a fit while limiting dissociative recombination to Na_2^+ molecules we believe that there are sufficient unknown rate coefficients in that model so that it can be done.

The third level of sophistication being investigated under this project is a model in which the assumption that the electron energy distribution is a Maxwellian is replaced by the simultaneous solution of the rate equations for the electrons in bound excited states and of the Boltzmann equation for the free electrons. Although the equations have been programmed and appear to be running properly, the problems of machine size and time and of the stability of the solution are severe. Because of the large amount of computer time required, this phase of the project is being carried out in an informal collaboration with Lawrence Livermore Laboratories.

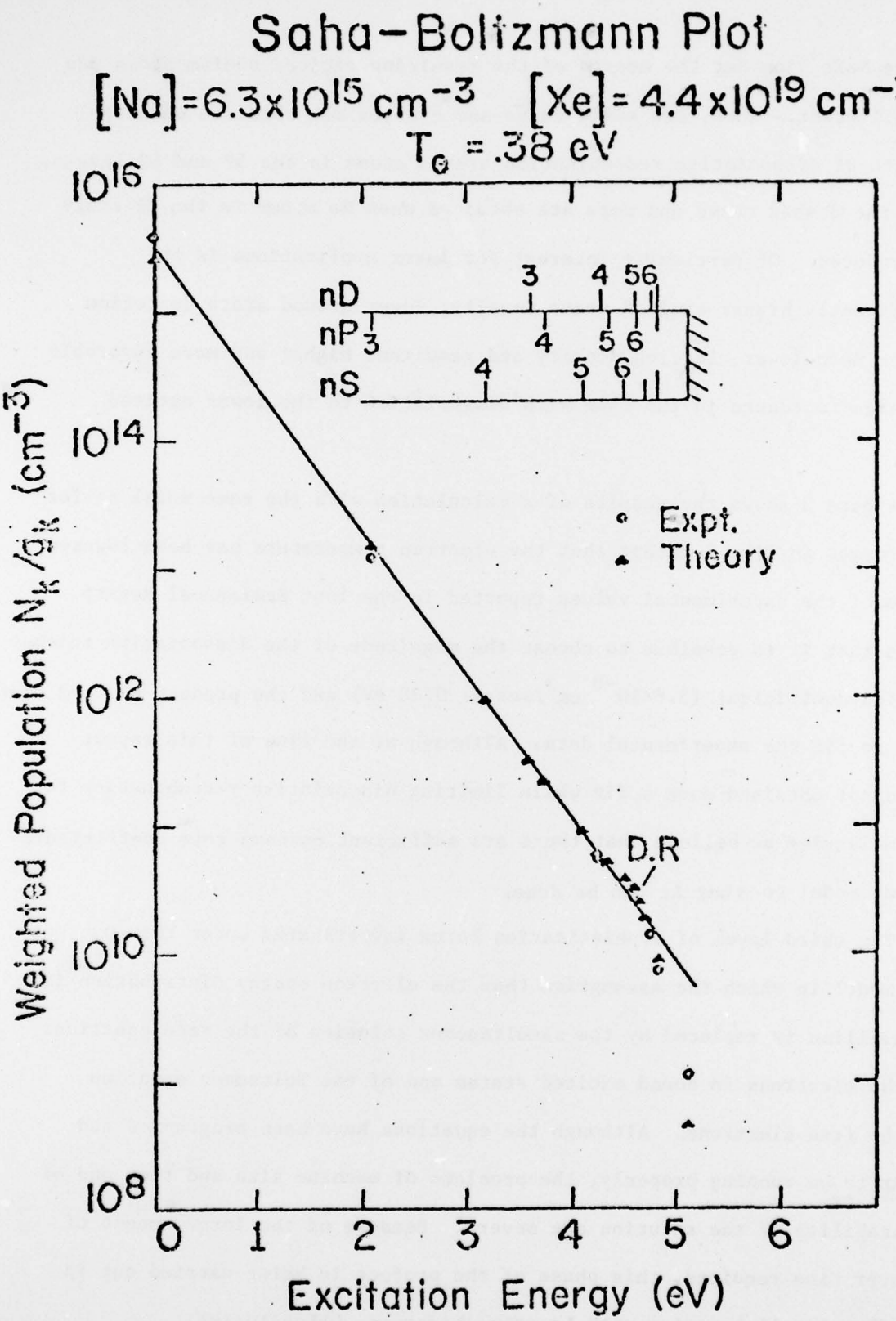


Figure 3. Experimental and calculated ground and excited state densities normalized to their statistical weights for [Na] = 6.3×10^{15} cm^{-3}, [Xe] = 4.4×10^{19} cm^{-3}, and T_e = 0.38 eV. The experimental data was obtained at a discharge current density of about 130 A/cm^2.

In summary, this work has shown that one can explain the close approach of the excited state and electron densities to Saha equilibrium values in NaXe discharges by reducing the energy loss and rate coefficients for dissociative recombination to values significantly below published values for atmospheric gases and heavy rare gases. It remains to be seen whether such adjustments can be made consistent with the measured energy dissipation, etc. in the discharge. Furthermore, it is crucial to the future utilization of electric discharge excitation in metal vapor based lasers that we obtain experimental data and predictive ability regarding the rates of and products of dissociative recombination for other metal vapor based systems. Although not yet included in our detailed models it is probable that predissociation of excited molecules contributes significantly to the deexcitation flow and energy dissipation in some of these discharges.

III. TRANSPORT OF RESONANCE EXCITATION IN GASES

A. Zajonc and A. V. Phelps.

The measurements of laser induced resonance fluorescence in high density sodium vapor designed to test models of the transport of resonance excitation were completed at the end of this report period. As shown in the last Semi-annual Report our theory of resonance excitation transport predicts a large decrease in the efficiency of laser induced fluorescence as the laser is tuned through the resonance line. Verification of these predictions has been obtained as shown by the data in Figs. 4 and 5. Figure 4 shows spectral scans of the fluorescence in the D_1 (589.6 nm) line of Na as the laser is tuned through the D_2 (589.0 nm) line. Except for the right-most line profile these line shapes are determined primarily by the resolution of the monochromator used to observe the fluorescence. As predicted by theory, the signal initially increases as

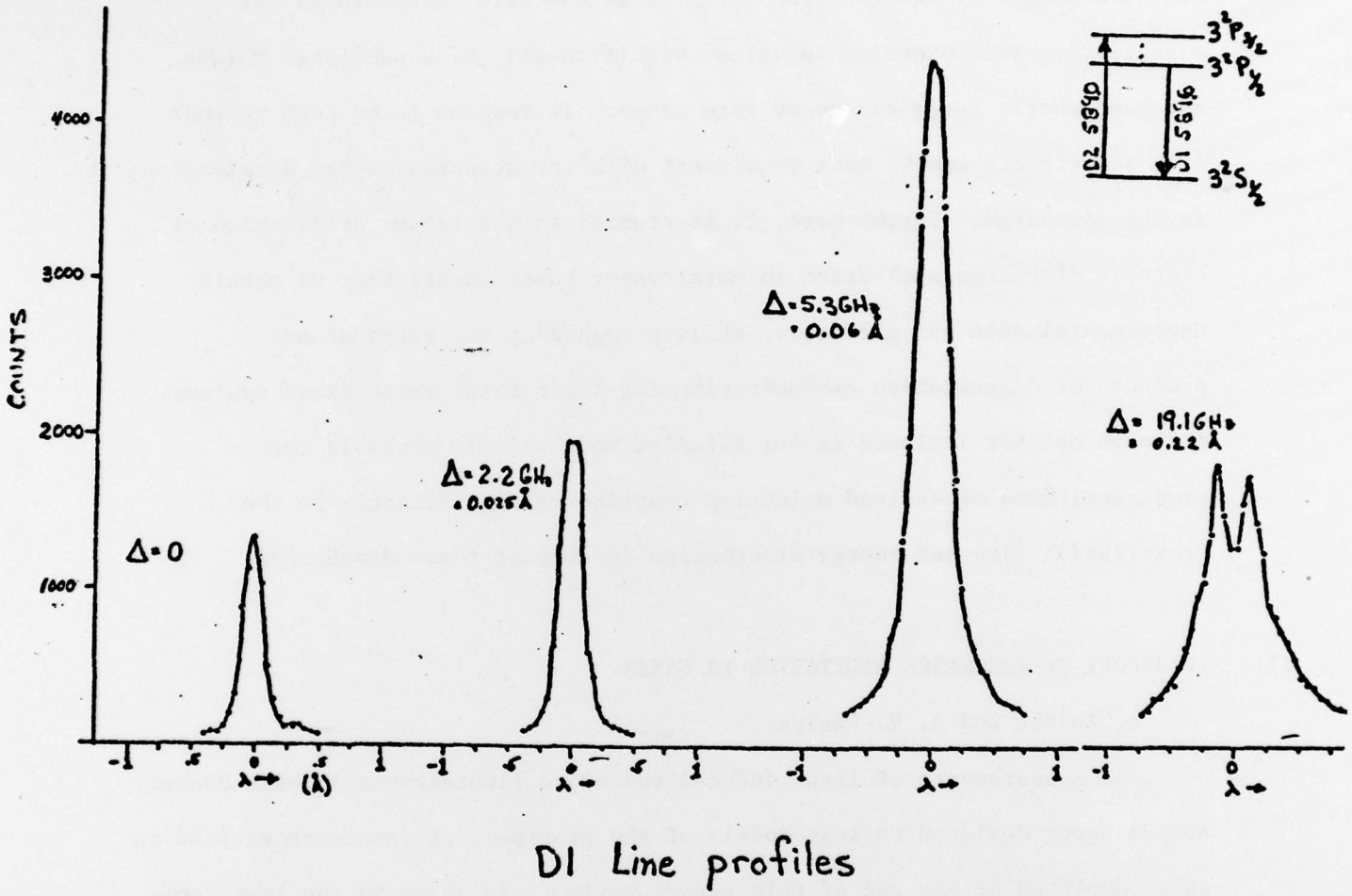


Figure 4. Profiles of Na D_1 fluorescence for various laser excitation frequencies relative to the center of the D_2 line. [Na] = 2.7×10^{15} cm^{-3} and T = 727 K.

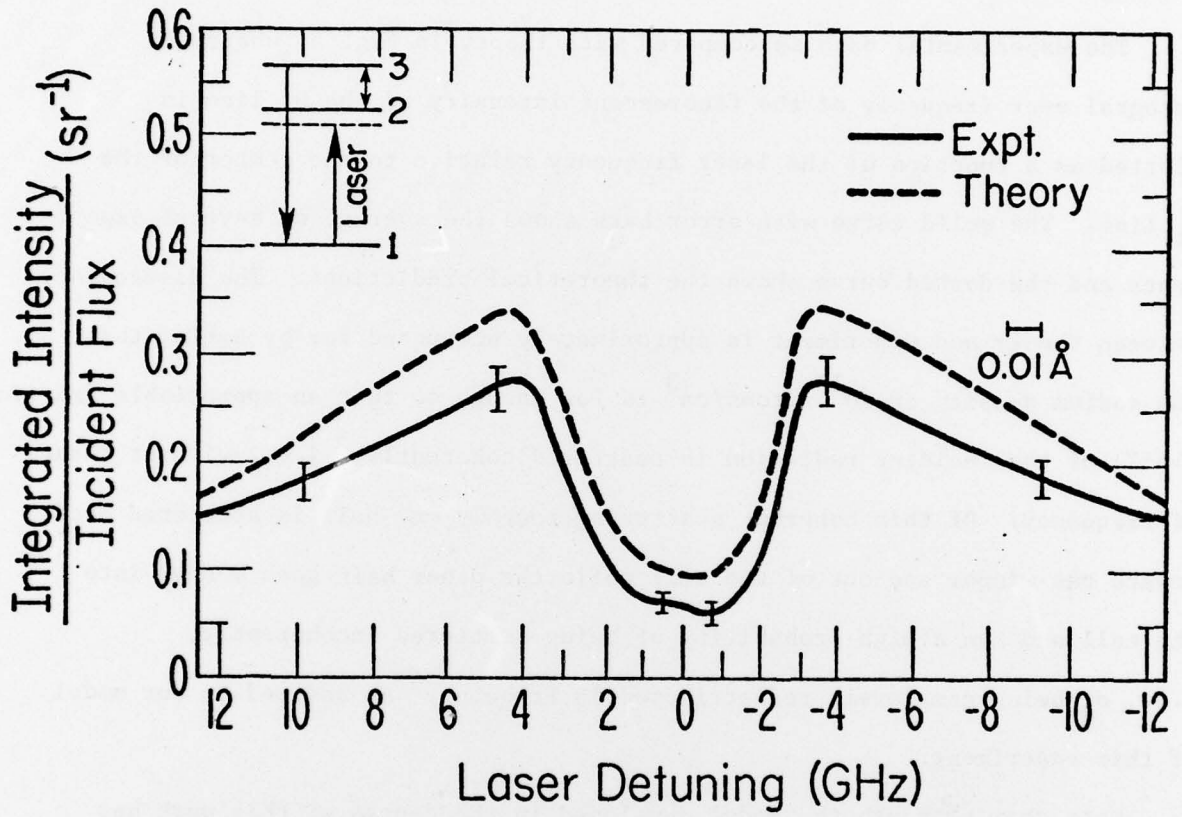


Figure 5. Sodium D_1 fluorescent intensity vs. laser frequency relative to center of D_2 line. [Na] = 10^{15} cm^{-3}.

the laser is tuned away from line center. At large detunings decreased absorption of the laser and self absorption of the fluorescence decreases the signal.

The experimental data is compared with theory in Fig. 5, where the integral over frequency of the fluorescent intensity of the D_2 line is plotted as a function of the laser frequency relative to the center of the D_1 line. The solid curve with error bars shows the average of several experiments and the dashed curve shows the theoretical predictions. The discrepancy between theory and experiment is approximately accounted for by noting that the sodium density of 10^{15} atoms/cm^3 is low enough so that an appreciable fraction ($\sim$55%) of the incident radiation is scattered coherently,[5] i.e., without change of frequency. Of this coherent scattering roughly one-half is scattered back toward the window and out of the cell while the other half goes deeper into the cell and has a high probability of being scattered incoherently, i.e., of being completely redistributed in frequency[4] as assumed in our model of this experiment.

Note that although the model developed in the course of this work has not been extended to high enough laser intensities to predict excited state saturation effects the nonradiative transport effects should raise significantly the threshold laser intensities required for saturation and the resultant spatial hole burning by the laser beam.

IV. ELECTRON EXCITATION OF METASTABLE ATOMS AND MOLECULES

D. Levron and A. V. Phelps.

During this report period measurements have been completed of the collisional relaxation and quenching of the two vibrational levels of the $N_2(A^3\Sigma_u^+)$ metastable state which are important to our determination of the

electron excitation rate coefficients for the N_2 ($A^3\Sigma_u^+$) state. The measured decay constants (reciprocal lifetimes) for the v=1 level and v=0 level of the N_2 ($A^3\Sigma_u^+$) state are shown in Fig. 6 as a function of the nitrogen density [N_2]. At low [N_2] the metastables are lost by diffusion to the electrodes of the drift tube. At the highest nitrogen densities we believe that the N_2 metastables in the v=0 level are deexcited to the ground state of N_2 in collisions with the $\sim 10^{-4}$% of O_2 molecules present as impurities in the gas sample. Using other investigators measurements of the ratio of quenching rate coefficients for the v=0 and v=1 levels of the N_2 (A^3) state by O_2 we can correct the decay constant data for the v=1 level and obtain the rate coefficient for the vibrational relaxation of the v=1 level to the v=0 level. Our rate coefficient of $(3.8 \pm 0.4) \times 10^{-17}$ cm^3/sec is two orders of magnitude larger than a previous estimate.

By making measurements of the radiation emitted by the v=0 level at rather high time resolution we are able to show that the collisionally deexcited v=1 metastables relax to the v=0 level of the N_2 ($A^3\Sigma_u^+$) state. This information is crucial to our determination of the total electron excitation rate coefficient for the N_2 metastables to be obtained during the next report period. These and similar results in Ar-N_2 mixtures will also be used in our measurements of electron excitation rate coefficients for Ar metastables.

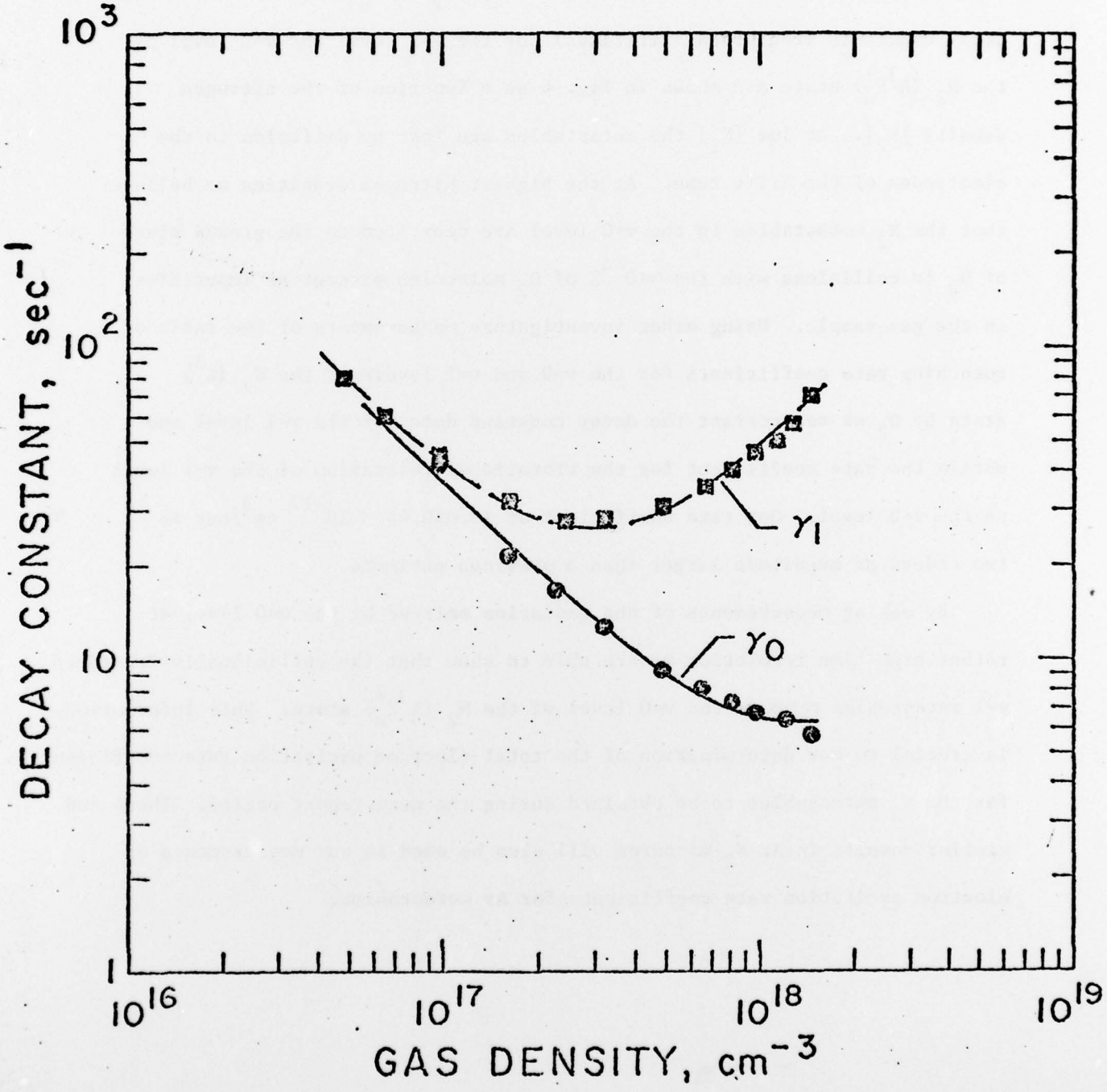


Figure 6. Measured decay constants for v=0 and v=1 vibrational levels of N_2 ($A^3\Sigma_u^+$) state vs. N_2 density. Curves are least-squares fits to data assuming loss by diffusion, radiation and quenching by N_2 or impurities.

REFERENCES

1. M. A. Biondi (private communication).

2. L. C. Johnson, Astrophysical J. 174, 227 (1972).

3. D. L. Moores, D. W. Norcross and V. B. Shorey, J. Phys. B 7, 371 (1974).

4. See, for example, D. R. Bates, Proc. Roy. Soc. (London) A337, 15 (1974).

5. A. Omont, E. W. Smith and J. Cooper, Astrophysical J. 175, 185 (1972).